

Electronic Spectra of Fluorobenzoic Acids

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The absorption and emission spectra of fluorobenzoic acids have been studied in different solvents, viz. water, ethanol and cyclohexane. The data are supplemented by theoretical calculation of electronic spectra by CNDO-S/CI method. The first excited singlet and triplet states of the acids are found to be of $^1\pi\pi^*$ and $^3\pi\pi^*$ -types respectively. The presence of these transitions accounts for the non-fluorescent and strongly phosphorescent nature of these compounds via coupling of $^3\pi\pi^*$ and $^1\pi\pi^*$. It is found that at low temperature (77K) all the isomers show weak fluorescence in water and ethanol. This is explained by hydrogen bonding of carbonyl oxygen with the solvent molecules.

The electronic spectra of fluorobenzoic acids do not seem to have been studied in detail and there is only one reference in the literature¹. As a part of our programme^{2,3} of systematic study of the electronic spectra of disubstituted benzenes, the electronic spectra of fluorobenzoic acids in different solvents have now been studied and the results supplemented by theoretical calculations of the spectra. The concentrations of benzoic acids are so chosen as to avoid the formation of dimeric species which may lead to complication in the interpretation of the spectra.

Materials and Methods

Ortho-, *meta*- and *para*-fluorobenzoic acids were prepared from corresponding fluorobenzaldehydes by oxidation with Jones' agent⁴, and the melting points of the fluorobenzoic acids (*ortho*- 394K, *meta*-396K and *para*-455K) agreed with the literature values.

Absolute ethanol was twice distilled over sodium metal and stored over molecular sieves. Water was distilled over potassium dichromate and potassium permanganate solutions. Cyclohexane⁵ was stirred with sulphuric acid, washed with water, dried over fused calcium chloride and distilled over sodium, b.p. 352.6K.

The UV spectra were obtained at room temperature with a Carl-Zeiss UV-VIS spectrophotometer. The fluorescence and phosphorescence spectra were taken on a Perkin-Elmer MPF-44B spectrophotometer.

Method of Calculation

The calculations were performed using a CNDO/S technique⁶ described previously and found suitable^{7,8} in describing the excited states of a variety of molecules. After the electron density on each atomic center had converged to within ± 0.005 electrons in SCF calculation, the excited configurations were generated and interacted (CI) to form the excited state.

For CI 30, lowest excited states were considered. The molecular axis and numbering of atoms are designated in Fig. 1. The values of the bond distances and bond angles were taken from literature^{9,10}.

The electron densities on various atoms in the excited state j were given by Eq. (1)

$$j\rho_A = {}^0\rho_A + \sum_m \sum_{\mu} C_{jm}^2 (C_{\mu f}^2 - C_{\mu i}^2) \quad \dots(1)$$

In which ${}^0\rho_A$ is the ground state electron density on atom A and C_{jm} being the coefficient of the m th configuration contributing to the j th state. $C_{\mu f}$ and $C_{\mu i}$ are respectively the orbital coefficients of the final and the initial molecular orbitals involved in the m th configuration contributing to the j th state. The characterization of the different states was done on the basis of configurational analysis. All the calculations were done on DEC-2050 machine.

Results and Discussion

The absorption and emission spectra of fluorobenzoic acids were recorded in different solvents, viz. water, ethanol and cyclohexane. The absorption spectra of all the isomers exhibit three moderate to very strong bands. The $\nu_{\max}$ (in kK) together with the oscillator strength (f) for all the isomers in different solvents are summarised in Table 1. The presence of an additional band near 33 kK could be detected only by taking their excitation spectra and hence its oscillator strength could not be calculated.

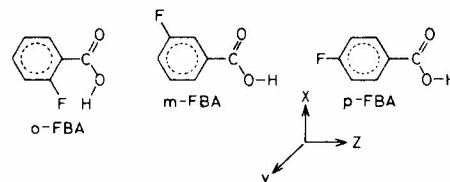


Fig. 1—Molecular axis designation [Y-axis being perpendicular to the molecular plane]

Table 1—Absorption and Emission Spectra of Fluorobenzoic Acids in Different Solvents

Water				Ethanol				Cyclohexane*	
$\nu_{\text{abs}}/\text{kK}$	f	ν_f/kK	ν_p/kK	$\nu_{\text{abs}}/\text{kK}$	f	ν_f/kK	ν_p/kK	$\nu_{\text{abs}}/\text{kK}$	ν_f/kK
<i>ortho</i> -Fluorobenzoic acid									
> 50.00	Intense band	—	—	> 50.00	Intense band	—	—	> 50.00	—
44.84	0.2540	—	—	44.64	0.2592	—	—	44.05	—
36.50	0.0215	—	—	36.20	0.0335	—	—	35.94	—
33.11	—	27.03	24.94	33.22	—	27.17	23.42	32.12	25.65
(exci)				(exci)				(exci)	
<i>meta</i> -Fluorobenzoic acid									
> 50.00	Intense band	—	—	> 50.00	Intense band	—	—	> 50.00	—
44.34	0.1785	—	—	44.15	0.3041	—	—	43.61	—
35.71	0.0243	—	—	36.07	0.0332	—	—	35.81	—
33.00	—	27.03	24.10	33.22	—	27.10	23.15	33.33	25.75
(exci)				(exci)				(exci)	
<i>para</i> -Fluorobenzoic acid									
> 50.00	Intense band	—	—	> 50.00	Intense band	—	—	> 50.00	—
43.88	0.3107	—	—	43.77	0.2700	—	—	42.91	—
38.17	0.0079	—	—	38.02	0.0075	—	—	37.88	—
32.56	—	27.28	24.10	33.68	—	27.25	23.15	34.48	26.20
(exci)				(exci)				(exci)	

*The oscillator strength (f) values in cyclohexane could not be calculated due to poor solubility of fluorobenzoic acids.

None of the isomer is fluorescent at room temperature but becomes fluorescent at lower temperature. All the three acids are strongly phosphorescent at 77K. The ν_f and ν_p are given in Table 1. The ν_f and ν_p values for water and ethanol refer to the acidic conditions to ensure that these values are for the undissociated acids. It is interesting to note that in Ethanol Propanol Acetone solvent at 77K, all the three isomers display two fluorescence maxima. This indicates the presence of two types of fluorescing species.

The calculated transition energies together with the oscillator strengths for all the isomers are given in Table 2. The molecular orbitals involved in the low energy transitions together with the orbital description for all the molecules are given in Table 3. The nature of the molecular orbitals are described by giving the symbols π , n ,....etc. The different monoexcited configurations which contribute to some of the low frequency transitions are given in Table 2. The calculated results predict the lowest excited state to be of $n\pi^*$ type for all the isomers near 28kK. As explained earlier this band is missing in the absorption spectra due to its low intensity and further it overlaps the strong $\pi\pi^*$ band (~ 36.5 kK). However, the theoretically predicted $n\pi^*$ band has been observed in the excitation spectra and the experimental values thus obtained agree with the theoretical values for all the three isomeric fluorobenzoic acids.

The next higher energy transition $S_0 \rightarrow S_2$ $\pi\pi^*$ (1_f) polarized along the short axis (X-direction) is assigned

to the observed band near 36.10 kK for the *ortho* and *meta*-fluorobenzoic acids while this band appears at a higher frequency (38.02 kK) forming a tail of the strongly allowed high energy band in *p*-fluorobenzoic acid. The next theoretically predicted transition $S_0 \rightarrow S_3$ (44.50 kK for *ortho*, 45.12 kK for *meta* and 44.28 kK for *para*) is attributed to observed bands at 44.64, 44.54 and 43.77 kK in *ortho*-, *meta*- and *para*-fluorobenzoic acids, respectively. This transition is $\pi\pi^*$ in character and is polarised along the long axis (Z-axis), hence is interpreted as 1L_a band. $S_0 \rightarrow S_4$ transition merges into the higher frequency side of this band. The intense band which is not clearly detected due to its occurrence beyond 50.00 kK comprised the theoretically predicted transitions $S_0 \rightarrow S_5$ to S_8 in *para* and $S_0 \rightarrow S_5$ to S_7 in *meta*- and *ortho*-fluorobenzoic acids. The agreement between the experimental and theoretical values of transition energies and other quantities seem to confirm that our assignments are correct.

Charge transfer nature of 1L_b and 1L_a bands

It can be seen from Table 1 that the frequencies of 1L_b and 1L_a bands increase with the polarity of the solvent. Normally the frequencies decrease for $\pi\pi^*$ transitions. Therefore, it was decided to calculate charges in the ground as well as both these excited states. The electron density calculated according to Eq. (1) for the benzene ring, fluoro group and carboxylic group are given in Table 4 for the 1L_b and 1L_a bands alongwith the electron density in the ground state. It is

Table 2—Electronic States of Fluorobenzoic Acids

$\nu_{\max}/\text{kK}$ In ethanol		Theoretical		Type	% CI	Composition
$\nu_{\max}/\text{kK}$	f	ν/kK	f			
<i>ortho</i> -Fluorobenzoic acid						
33.22	—	27.38	—	mix	51	24→27
					31	26→28
					4	22→27
36.20	0.0335	36.54	0.0045	$\pi\pi^*$	21	26→27
					62	25→27
					13	25→28
44.64	0.2592	44.51	0.0960	mix	36	26→27
					18	25→27
					45	24→28
		47.19	—	mix	29	26→27
					13	25→27
					10	25→28
				mix	46	24→28
—	—	48.76	—		39	24→27
					16	26→28
				mix	7	26→29
					5	23→28
					11	22→29
				$\pi\pi^*$	13	25→32
> 50.00	Intense band	51.43	0.4279		12	26→27
					6	25→27
				mix	69	25→28
					6	24→28
		51.90	0.4578		71	24→29
				10	22→28	
<i>meta</i> -Fluorobenzoic acid						
33.22		28.43	—	mix	50	24→27
					21	26→28
					14	24→28
				$\pi\pi^*$	8	21→27
36.07	0.0332	36.66	0.0037		40	25→27
					23	26→27
				$\pi\pi^*$	27	25→28
					7	22→27
44.15	0.3041	45.12	0.1058		16	25→27
				58	26→27	
				25	22→27	
		47.70	—	$\pi\pi^*$	31	25→27
					4	24→27
					55	25→28
				mix	4	22→27
		50.12	—		40	24→27
					10	26→28
				mix	10	24→28
					6	21→27
					6	23→28
				mix	5	26→31
					18	23→29
> 50.00	Intense band	50.95	0.4185		10	25→27
				15	26→27	
				11	25→28	
				61	22→27	
<i>para</i> -Fluorobenzoic acid						
33.68		28.21	—	mix	51	24→27
					21	26→28
					14	24→29

(Contd)

Table 2—Electronic States of Fluorobenzoic Acids—(Contd.)

In ethanol		Theoretical		Type	% CI	Composition
$\nu_{\max}/\text{kK}$	f	ν/kK	f			
38.02	0.0076	36.74	0.0010	$\pi\pi^*$	51	25→27
					39	25→28
					9	22→28
43.77	0.3307	44.28	0.1687	$\pi\pi^*$	88	26→27
					9	22→28
					45	25→27
		48.98	—	$\pi\pi^*$	38	25→28
					13	22→28
					40	24→27
		50.10	—	mix	10	26→28
					8	24→29
					12	21→27
					12	22→29
> 50.00	Intense band	51.57	—	mix	10	22→30
					44	26→28
		51.80	0.3263	mix	49	24→29
					11	26→27
					18	25→28
					64	22→28
					7	22→27
		52.76	0.5216	$n\pi^*$	89	24→28

Table 3—Description of Molecular Orbitals of Fluorobenzoic Acids Involved in the Lowest Energy Transitions

MO	<i>o</i> -Fluorobenzoic acid		<i>m</i> -Fluorobenzoic acid		<i>p</i> -Fluorobenzoic acid	
	Energy (eV)	Description	Energy (eV)	Description	Energy (eV)	Description
22	−12.589	σ_{del}	−12.458	σ_{del}	−12.450	σ_{del}
23	−11.746	$\pi_{\text{C}_1\text{C}_2\text{C}_3\text{C}_6\text{COO}}$	−11.855	$\pi_{\text{C}_1\text{C}_2\text{C}_3\text{C}_6\text{COO}}$	−11.823	$\pi_{\text{C}_1\text{C}_2\text{C}_3\text{C}_6\text{COO}}$
24	−10.561	$n_{\text{C=O}}$	−10.783	$n_{\text{C=O}}$	−10.746	$n_{\text{C=O}}$
25	−10.108	π_{rO}	−10.088	π_{del}	−10.204	$\pi_{\text{C}_2\text{C}_3\text{C}_6}$
26	−9.903	$\pi_{\text{C}_1\text{C}_2\text{C}_3\text{C}_6\text{F}}$	−9.987	$\pi_{\text{C}_1\text{C}_2\text{C}_3\text{C}_6\text{F}}$	−9.897	π_{del}
27	−1.280	π^*_{rCOO}	−1.299	π^*_{del}	−1.326	π^*_{del}
28	−0.821	$\pi^*_{\text{C}_2\text{C}_3\text{C}_6}$	−0.834	$\pi^*_{\text{C}_2\text{C}_3\text{C}_6}$	−0.812	$\pi^*_{\text{C}_2\text{C}_3\text{C}_6}$
29	−0.804	π^*_{rCOO}	0.703	π^*_{rCOO}	0.690	π^*_{rCOO}

Subscripts: r signifies that the orbital is localised on the benzene ring only; del means that the orbital is delocalised over the entire molecule.

obvious from Table 4 that for the 1L_b band the charge is transferred from ring to carboxylic group (in *ortho* isomer, there is some charge transfer from fluoro group also, probably due to hydrogen bonding). This is in conformity with the observation that the acidic nature of the carboxylic group decreases¹⁰ in the excited state. Theoretical results indicate that pK for 1L_a state should be less than that for the ground state for *ortho*-fluorobenzoic acid. The charge transfer for the *meta*- and *para* isomers in the 1L_a state is comparatively less than that in 1L_b state. In the *meta*-isomer the charge is transferred from the fluoro group to the carboxylic group while for the *para*-isomer the charge is transferred both from ring and fluoro group to the carboxylic group.

Table 4—Ground and Excited State Charge Densities in Fluorobenzoic Acids

State	Ring	COOH group	F group	Remarks
<i>ortho</i> -Fluorobenzoic acid				
S_0	0.286	−0.083	−0.204	CT from ring to the
$S_2(^1L_b)$	0.354	−0.159	−0.195	−COOH group
$S_3(^1L_a)$	−0.040	0.230	−0.193	CT from −COOH group to the ring
<i>meta</i> -Fluorobenzoic acid				
S_0	0.312	−0.098	−0.215	CT from ring to the
$S_2(^1L_b)$	0.350	−0.149	−0.204	−COOH group
$S_3(^1L_a)$	0.320	−0.119	−0.197	
<i>para</i> -Fluorobenzoic acid				
S_0	0.310	−0.097	−0.214	CT from ring to the
$S_2(^1L_b)$	0.383	−0.175	−0.219	COOH group
$S_3(^1L_a)$	0.325	−0.132	−0.195	

Emission

For the monomer the lowest excited singlet is of $n\pi^*$ and as mentioned earlier at room temperature all the

isomeric fluorobenzoic acids are non-fluorescent. In fact very few compounds with $^1n\pi^*$ are known^{12,13} to be fluorescent. However, at low temperature (77K) all the three acids are weakly fluorescent. The fluorescence in the non-polar solvent is probably due to dimer formation. However, in polar solvent (water or ethanol) the dimer formation is very small. Therefore, we suggest that the fluorescent species is the fluorobenzoic acid hydrogen-bonded to the solvent through the oxygen of its carbonyl group. This leads to a decrease in energy of $\pi\pi^*$ transition. The $^1n\pi^*$ state should increase in energy because the stabilization of ground state by the hydrogen bond is greater than that of the excited state where the oxygen has lost non-bonding electron density. This is supported by the two fluorescence maxima around 27.3 and 25.6 kK in Ethanol Propanol Acetone solvent at 77 K. The position of the first maximum is exactly the same when ethanol is used as a solvent. Thus it is not the vibrational structure of the second fluorescence band at 25.6 kK. The position of the second maximum tallies with the ν_f for fluorobenzoic acid in non-polar solvents and is attributed to the formation of dimer. Thus in EPA both the monomer and the dimer of fluoro-benzoic acids exist.

The observation of Baba and Kitamura¹⁴ that benzoic acid is non-fluorescent in isopentane + methyl cyclohexane at low temperature in the presence of ether is also consistent with our arguments and observations. Here, the hydrogen bond is formed between the hydroxyl group of acid and the oxygen of

the ether, leaving the non-bonding electron of the carbonyl group unutilized. The lowest excited singlet state here is still $n\pi^*$ type.

For *ortho*-, *meta*- and *para*-fluorobenzoic acids the lowest triplet states are calculated to be of $\pi\pi^*$ type and occur at 22.56, 22.68 and 22.51 kK, respectively. This is in good agreement with the experimental values in ethanol (23.42 kK for *ortho*, 23.15 kK for *meta*- and 23.15 kK for *para*-isomers).

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References

- 1 Forbes W F & Sheratle M B, *Can J Chem*, **33** (1955) 1829.
- 2 Jain D V S, Nandel F S & Lata P, *Indian J Chem*, **21A** (1982) 559.
- 3 Jain D V S, Nandel F S & Lata P, *Indian J Chem* (in press).
- 4 Welch S C, Hagan C P, Kim J H & Chu P S, *J Org Chem*, **42** (1977) 2879.
- 5 Riddick J A & Bunger W B, *Organic solvents, physical properties and methods of purification* (Wiley Interscience, New York), 197.
- 6 174 Quantum Chemistry program exchange, (Indiana University, Bloomington, Indiana).
- 7 Del Bene J & Jaffe H H, *J chem Phys*, **48** (1968) 1807.
- 8 Ellis R L, Kuehnlenz G & Jaffe H H, *Theoret Chim Acta* (Berlin), **26** (1972) 131.
- 9 Ferguson G & Islam K M S, *Acta Cryst*, **21** (1966) 1000.
- 10 Krausse J & Dunker H, *Acta Cryst*, **20** (1966) 67.
- 11 Vander Doncket E, *Progr React Kinetics*, **5** (1970) 273.
- 12 Lower S K & El-Sayed M A, *Chem Rev*, **66** (1966) 199.
- 13 El-Sayed M A, *J chem Phys*, **38** (1963) 2834.
- 14 Baba H & Kitamura M, *J molec Spectr*, **41** (1972) 302.